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CANADIAN JOURNAL OF TECHNOLOGY

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PENETRATION OF CHLORTETRACYCLINE INTO FISH MUSCLE AND ITS DESTRUCTION BY HEAT¹

BY G. STEINER AND H. L. A. TARR

ABSTRACT

The concentrations of chlortetracycline (CTC) in flesh of fish iced with ice containing 1 $\mu\text{gm./gm.}$ of the antibiotic, or held in refrigerated sea water containing 2.8 $\mu\text{gm./gm.}$, were determined by microbiological assay. With iced fish relatively small amounts penetrated the fish, and these occurred largely in the visceral cavity walls and especially in samples in which the skin was not removed. Fish stored in sea water containing CTC absorbed the antibiotic more markedly than did those stored in ice, and with these also the skin and visceral cavity walls had the highest concentrations. Destruction of CTC in fish flesh was determined in samples heated to 60°, 82°, and 99°C.

Experiments indicate that chlortetracycline (CTC) is probably by far the most effective antibacterial agent yet discovered for fish preservation (4, 5, 6, 7, 8, 9). However, the amounts of CTC which are absorbed by whole or eviscerated fish stored in ice or in refrigerated sea water containing only a few micrograms per gram of the antibiotic have not been determined successfully. Also, destruction of CTC in heated fish muscle has been studied only to a very limited extent (7). Work on these problems has been delayed because it has been found that extracts of normal muscles of many species of fish give inhibition zones in the usual pad plate microbiological assay for this antibiotic. The finding that flesh extracts of gray cod (*Gadus macrocephalus*) only give such fictitious assays occasionally has facilitated experimental work on the above problems.

EXPERIMENTAL

Gray cod which had been iced on fishing boats for one or two days were eviscerated and washed lightly with running tap water. They were then iced thoroughly in galvanized containers placed in an insulated box (7), one group with ordinary crushed block ice and another with similar ice containing 1 $\mu\text{gm./gm.}$ of CTC distributed by the carboxymethylcellulose - sodium chloride method (1). In another experiment similar fish were stored in refrige-

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Contribution from the Fisheries Research Board of Canada, Pacific Fisheries Experimental Station, Vancouver 2, B.C.

rated circulating sea water at $-1^{\circ} \pm 0.5^{\circ}\text{C}$. with and without $2.8 \mu\text{gm./ml.}$ of CTC.

At intervals fish were removed from their respective treatments. They were filleted without washing and only one of the fillets was skinned. Two samples were taken from each fillet, one from near the tail and the other from the visceral cavity wall and including the membrane lining of the visceral cavity. The samples were blended promptly with twice their weight of distilled water and sufficient 2.5 N HCl to adjust the suspension to pH 4.5. They were centrifuged at about $20,000g$ and at 0°C ., the supernatant liquids being promptly frozen until microbiological assays could be made. The pad plate microbiological assay for CTC described by Broquist and Kohler (2) was used. This method is not usually sensitive to much less than $0.01 \mu\text{gm.}$ of CTC per 0.5 in. filter paper assay disk. Since 0.1 ml. of a $1:3$ dilution of fish muscle was applied to each pad the limit of sensitivity of the assay was generally assumed to be $0.3 \mu\text{gm.}$ of CTC per gram of muscle and was never more than $0.2 \mu\text{gm.}$ per gram.

The results of two similar experiments made to ascertain the amount of CTC penetration occurring with iced fish are given in Table I. It will be seen

TABLE I
PENETRATION OF CTC INTO EVISCERATED GRAY COD STORED
IN ICE CONTAINING $1 \mu\text{GM./GM.}$ OF THE ANTIBIOTIC

Section of fish*	CTC in $\mu\text{gm./gm.}$ after days†							
	0	1	2	3	4	5	7	10
Ordinary ice								
V+S	0 0	0 0	0 0	0 0	0	0	0 0	0.2 0
V-S	0 0	0 1.1	0 0	0 0	0	0	0 0	0 0
T+S	0 0	0 0	0 0	0 0	0	0	0 0	0.2
T-S	0 0	0 0	0 0	0 0.5	0	0	0 0	
CTC ice								
V+S		0 0	0 0	0 1.1	0	0	0.39 0.30	0.9 0.5
V-S		0 0	0 0	0.45 0	0	1.3	0.54 0.30	0.7 0.3
T+S		0 0	0 0	0 0	0	0	0 0	0 0.8
T-S		0 0	0.6 0	0 0	0	0	0 0	0 0

*V+S = Visceral cavity wall with skin.

V-S = Visceral cavity wall without skin.

T+S = Tail end of fish with skin.

T-S = Tail end of fish without skin.

†0 = $< 0.3 \mu\text{gm./gm.}$

that fictitious CTC assay results such as occur with many species of fish are found only very occasionally with gray cod. In general it appears that, in fish iced with ice containing CTC, the antibiotic occurs largely in samples containing skin and especially in those taken from the thin visceral cavity walls, and is found regularly only after the fish have been over five days in the ice. During the first five days in CTC ice there is only occasional erratic penetration, and since a few of the samples taken from fish from ordinary ice gave fictitious assays, it is possible that certain of the positive results obtained with fish from CTC ice may have been due in part or entirely to a similar cause.

The results obtained with fish held in refrigerated sea water containing CTC (Table II) showed that definite penetration occurred earlier than with fish held in CTC ice, but that with these also the visceral cavity wall and skin

TABLE II

PENETRATION OF CTC INTO EвисCERATED GRAY COD STORED IN ORDINARY SEA WATER AND IN SEA WATER CONTAINING 2.8 $\mu\text{GM.}/\text{GM.}$ OF THE ANTIBIOTIC

Section of fish*	CTC in $\mu\text{gm.}/\text{gm.}$ after days*						
	0	1	2	4	5	6	7
Ordinary sea water							
V+S	0		0		0		0
V-S	0		0		0		0
T+S	0		0		0		0
T-S	0		0		0		0
Sea water with CTC							
V+S		1.5	3.0	1.5		2.16	3.0
V-S		0	1.23	1.23		1.26	1.14
T+S		1.2	1.5	1.5		1.26	2.55
T-S		0	0	0		0	0

*As in Table I.

containing samples had the higher concentrations. It is of interest that the muscle from the tail region without skin gave no positive assay for CTC even after seven days' storage.

The effect of different heating times and temperatures on destruction of CTC in fish muscle was determined as follows: Muscle from a strictly fresh gray cod was blended with an equal quantity of distilled water, or CTC solutions containing 10 and 20 $\mu\text{gm.}/\text{ml.}$ of the antibiotic, the pH of the blends being 6.5. Twelve gram amounts of the suspension were centrifuged at 3°C. in 15.8×762 mm. stainless steel tubes at 26,000g in a Spinco preparative ultracentrifuge, the supernatant liquids being discarded.

The samples were stored at -20°C. for a few days until required. The temperature of the samples was then adjusted to between 0° and 1°C. and a thermocouple inserted in the center of the contents of each tube. Microbiological assays showed that the untreated flesh samples both before and after heating (*vide infra*) contained no measurable CTC. Samples con-

taining CTC were placed in water baths maintained at temperatures a few degrees above those to which the fish were to be heated, namely 60°, 82°, and 99°C. One series was heated until the desired temperature was attained, and another for five minutes after this temperature was reached. The tests were conducted in duplicate or in triplicate (Table III). After heating, the samples were frozen promptly in a bath of solid carbon dioxide and methanol.

TABLE III
INACTIVATION OF CHLORTETRACYCLINE ON HEATING FISH FLESH CONTAINING
6.5 AND 16.0 $\mu\text{gm./gm}$ OF THE ANTIBIOTIC

Temperature (°C.)	Time required to attain temperature	CTC content ($\mu\text{gm./gm.}$)	Time required to raise and maintain temperature 5 min.	CTC content ($\mu\text{gm./gm.}$) after holding 5 min. at temp. given
6.5 $\mu\text{gm./gm.}$ CTC*				
60	5 min. 40 sec.	1.4	11 min. 45 sec.	1.4
	6 " 10 "	1.2	11 " 0 "	1.8
82	5 " 29 "	1.4	11 " 35 "	1.8
	8 " 0 "	1.8	15 " 0 "	1.2
99	5 " 8 "	<0.3	10 " 0 "	<0.3
	4 " 50 "	0.8	10 " 30 "	<0.3
16.0* $\mu\text{gm./gm.}$ CTC				
60	8 " 45 "	13.2	12 " 35 "	2.8
	8 " 45 "	11.2	12 " 35 "	2.8
	8 " 45 "	11.2	12 " 35 "	2.8
82	9 " 27 "	6.6	16 " 0 "	2.0
	9 " 27 "	5.4	16 " 0 "	3.0
	9 " 27 "	4.8	16 " 0 "	2.4
99	14 " 0 "	2.4	10 " 35 "	0.98
	14 " 0 "	2.4	10 " 35 "	1.2
	14 " 0 "	2.4	10 " 35 "	0.92

*Determined by microbiological assay of unheated samples.

They were kept frozen for several days until microbiological assays could be made to determine the CTC content. The extraction method used was similar to that recorded above except that an equal volume of water was used.

The results (Table III) indicate that at 60° and 80°C. there is about the same degree of destruction of CTC, and that this is not appreciably increased by heating for five minutes after the temperature is attained. In samples heated to 99° there was a much more marked destruction of CTC and further destruction occurred when the samples were kept an additional five minutes at this temperature.

DISCUSSION

The results have shown that gray cod rarely contains indigenous substances which cause fictitious CTC assay results. These fish, when stored in ice containing 1 $\mu\text{gm./gm.}$ of the antibiotic, absorb small amounts after about five days, but this occurs mainly in the thin visceral cavity walls and in the skin. As yet the average CTC content of whole eviscerated fish so iced has not been determined, but it is doubtful if it would exceed 0.01–0.2 $\mu\text{gm./gm.}$ after normal storage periods not exceeding 10 days.

It has long been recognized that CTC is unstable, especially when stored in dilute solutions at pH values above 4.5, and also when subjected to heating. The protective effect exerted by various colloids and other naturally-occurring substances against heat destruction of CTC has also been recorded (3). Isoaureomycin, which was first isolated from CTC following alkali treatment (10), is also formed when flesh foods containing the antibiotic are heated.* It is apparently inert, or almost inert, bacteriostatically (3).

The present work has shown that heating, such as could occur in the usual rather mild cooking procedures advocated for fish, destroys a very large percentage of the CTC as judged by microbiological assays.

The nature of the residual antibacterial activity occurring in heated fish flesh has not as yet been determined, but it could be due to CTC itself which has been protected by fish muscle constituents, or to a degradation product which has antibacterial activity. The latter assumption would appear unlikely since isoaureomycin, which is probably formed on heating CTC-containing fish flesh, reportedly has little antibacterial activity (3). It remains to be determined whether detectable CTC residues occur in fish which have been iced with CTC-containing ice and have subsequently been cooked by normal procedures.

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*L. R. Hines. Private communication.

THE PREPARATION OF SODIUM ALGINATE FROM ROCKWEED¹

By D. L. VINCENT

ABSTRACT

Various methods of extracting alginate from the rockweed and kelp of Nova Scotia have been tried. By the usual methods the product developed a light brown color during treatment with basic media. A colorless product was obtained with little or no loss of viscosity by (1) passage of the crude solution of alginate through a carbon-Celite column, (2) carefully controlled bleaching with sodium hypochlorite, (3) exhaustive extraction of the weed with methanol prior to extraction of alginate. Extraction of the dried plant at 10°-23°C. followed by precipitation with ethanol furnished an alginate of higher viscosity than by the usual procedure. In general, yields and quality of product were lower from rockweed than from kelp.

INTRODUCTION

Sodium alginate is usually produced commercially from various species of kelp, such as *Laminaria*, *Macrocystis*, and *Nereocystis* (7, 8). It may also be obtained with more difficulty from common rockweeds such as *Fucus vesiculosus* and *Ascophyllum nodosum*, although the product and yield are inferior (1, 4, 10). For many industrial purposes a high grade alginate is not required, and the main purpose of the present investigation was to determine whether a satisfactory product could be readily obtained from the local rockweed.

EXPERIMENTAL

Source and Treatment of Seaweeds

Specimens of *F. vesiculosus* and *L. digitata* were collected at Halifax in August and September, rinsed twice with tap water, air-dried at 20°-25°C., and ground in a Wiley mill to pass through a 40 mesh sieve.

Basic Method of Preparation of Sodium Alginate

The method of extraction was essentially that of Rose (10). Ten grams of powdered plant were stirred at 60°C. for 30 min. with 200 ml. of water containing 0.5 gm. of calcium hydroxide. After alternate centrifuging and washing three times with 1 liter of water at about 23°C., the weed was stirred for 30 min. with 200 ml. of 0.2 *N* sulphuric acid. After centrifuging and washing twice with 1 liter of water, it was digested with 100 ml. of 3% sodium carbonate for two hours at 50°C. with mechanical stirring, diluted to 600 ml. with water, and stirred for three hours longer. The mixture was allowed to stand overnight, centrifuged, and the residue washed twice with 1 liter of water. The combined centrifugates were filtered through a bed of Celite in a coarse sintered glass funnel, then decolorized or bleached if desired. The resulting solution was slowly poured, with stirring, into 100 ml. of 25%

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calcium chloride solution and stirred for 30 min. The calcium alginate was removed on a sintered glass funnel, washed with water containing 5% ethanol, and treated on the funnel with 0.5 *N* hydrochloric acid at 10°C. for not over 30 min., in several portions to a total volume of about 3 liters. The product was washed several times with 50% ethanol until free from hydrochloric acid, then with 95% ethanol and ether. The alginic acid was dried *in vacuo* over phosphorus pentoxide until constant weight was attained. When sodium alginate was the desired product, the alginic acid was dissolved in a minimum amount of dilute sodium hydroxide at room temperature and precipitated with four volumes of ethanol. The sodium alginate was filtered through a sintered glass funnel, washed with ethanol until free of sodium hydroxide, then with ether, and dried *in vacuo* over phosphorus pentoxide.

Analytical Methods

Color, viscosity, percentage of alginate, and sulphated ash were taken as criteria of quality.

Viscosities were measured at 25°C. on 0.25% (w/w) solutions of sodium alginate in 0.1 *N* sodium chloride to eliminate the electroviscous effect (5, 10). Solutions were generally prepared by weighing out the sodium alginate. Unless stated otherwise, a No. 1 B.S.I. viscometer was used below 5 cs., and a No. 2 viscometer above 5 cs., calibrated by standard methods (2). Apparent viscosities were thus measured under the specified conditions, since viscosities of alginate solutions vary with the rate of shear (1).

The percentage of alginate was determined either by direct titration of the dried alginic acid with 0.05 *N* sodium hydroxide or by the calcium acetate method of Cameron, Ross, and Percival (3).

The percentage of sulphated ash was determined by twice ashing the sample at about 900°C. with a few drops of concentrated sulphuric acid. The theoretical value for sodium alginate is 35.86%.

Decolorization

Various agents were used in attempts to decolorize the solutions of crude sodium alginate prior to precipitation. These included activated carbon, diatomaceous earth (Celite), magnesium silicate (Magnesol), magnesium carbonate, alumina, aluminum hydroxide gel, silica gel, and ion exchange resins.

Carbon

By stirring carbon (Darco G-60) into the solution of crude sodium alginate overnight and adding successive fresh portions it was possible to render the solution colorless. About 70 gm. were required for 10 gm. of dried seaweed. The suspending power of alginate made removal of the last traces of carbon difficult, and preliminary centrifugation, followed by slow filtration through paper pulp, was required. By stirring the crude extract overnight with carbon in a ratio of one part of alginate to four of carbon, followed by the above clarification, a pale yellow solution was obtained. This was completely decolorized by passage through a column (260×74 mm.) containing a 1:3

mixture of Darco G-60 and Celite 535 which rested on a layer ($\frac{1}{2}$ in.) of Celite 535 and this on a layer (2 in.) of paper pulp. The yield however was poor.

Other Adsorbents

A mixture of Celite-Magnesol (1:5) or magnesium carbonate alone was moderately effective. Magnesol in the proportion of 1 to 10 of dried plant gave a pale ivory product with a viscosity of 5.8 cs. in a yield of 16.4%. Neither alumina gel nor silica gel was notably effective. Only slight decolorization was obtained by passage through columns of IRA-410, Dowex-2, or Duolite S-30 resins.

Formaldehyde

The residue after lime and acid extractions was steeped in formaldehyde (40%) for two hours, drained, and stored for four weeks. Subsequent extraction with sodium carbonate furnished a product only slightly less colored than if formaldehyde had been omitted. Longer treatment was no more effective.

Preliminary Solvent Extraction

When moist freshly prepared alginic acid was extracted with ethanol (95%), considerable color was removed but this was not found to apply to preparations which had been dried. Extraction of the dried plant with ethanol in a Soxhlet apparatus for 24 hr. followed by ether for four hours removed much color. This procedure however failed to improve the final product of sodium alginate appreciably. The results of preliminary extraction with various solvents for 30 days are shown in Table I. Prolonged extraction with methanol or ethanol was effective in permitting the preparation of a white alginate by the basic method with extraction by sodium carbonate at 23°C.

TABLE I
EFFECT OF PRELIMINARY SOLVENT EXTRACTION OF *F. vesiculosus* ON PROPERTIES OF SODIUM ALGinate

Solvent	Color of sodium alginate	Yield, % of air-dried weed	Viscosity, cs.*
Ethanol	White	8.8	5.6
Methanol	White	15.8	3.0
Benzene	Light brown	16.5	2.8
Ether	Light brown	16.7	3.7
2:1 Benzene-ethanol	Pale ivory	16.5	5.6
Water	Light brown	2.4	1.2

*No. 1 B.S.I. viscometer for all values.

*Effect of Method of Preparation of Properties of Alginate from *F. vesiculosus**

Fifty grams of dried weed were extracted by the basic method, and the extract was completely decolorized by passage through a carbon-Celite column. The solution was divided into four parts. (A) Ethanol was added to establish a concentration of 75% and after 1.5 hr. the fibrous precipitate was filtered on a medium sintered glass funnel, washed, and dried. (B) Dilute

hydrochloric acid was added at 23°C. to establish pH 2. The gelatinous precipitate was centrifuged down, washed free of acid with ethanol, then washed with ether and dried. (C) Calcium alginate was precipitated with 25% calcium chloride. The precipitate was leached for 30 min. on a coarse sintered glass funnel with 0.5 *N* hydrochloric acid at 23°C. until all calcium was removed. The alginic acid was washed free of chloride and dried as usual. (D) This portion was treated as in (C), except that the leaching with acid was done at 10°C. The results are shown in Table II. The product precipitated directly with ethanol was least pure but had the highest viscosity. The best method of purification was the standard one of precipitating the alginate as the calcium salt and converting it to free alginic acid with cold dilute hydrochloric acid for as short a time as possible.

TABLE II

EFFECT OF METHOD OF PREPARATION ON PROPERTIES OF ALGINATE FROM *F. vesiculosus*
Alginate was extracted by the basic method, decolorized by passage through a carbon-Celite column, and the solution divided into four parts

Method	Yield of alginic acid, % of air-dried weed	Viscosity, cs.	Purity, % alginic acid in dried product
(A) Precipitated with ethanol	7.0	13.9	76.6
(B) Precipitated with hydrochloric acid at 23°C.	3.5	4.0	92.9
(C) Precipitated with calcium chloride, leached with hydrochloric acid at 23°C.	4.2	3.6	95.4
(D) As in (C), but leached at 10°C.	5.3	6.1	90.8

Effect of Method of Preparation on Properties of Alginate from L. digitata

Fifty grams of dried weed were extracted by the basic method. The extract was clearer and less colored than that from *F. vesiculosus*, and no additional color developed during the digestion with sodium carbonate as it did with the rockweed. One third of the resulting pale yellow solution was divided into two parts, one of which (A) was precipitated with ethanol and the other (B) with calcium chloride, followed by leaching with hydrochloric acid at 10° for 30 min. The remainder was decolorized completely by stirring overnight with Darco G-60 and the carbon removed as previously described. The decolorized portion was divided into three parts, the first of which (C) was precipitated with ethanol, the second (D) with calcium chloride, followed by leaching with dilute hydrochloric acid at 10°C. for 30 min., and the third (E) was precipitated with dilute hydrochloric acid, the precipitate removed by centrifugation, and washed and dried as usual. The results are shown in Table III. Higher yields were obtained than with *F. vesiculosus*, and the products which had received no decolorizing treatment were nearly white. Precipitation with ethanol gave the highest yield but the least pure product. Lower yields were obtained from the decolorized aliquots. Viscosities were lower than would be expected for alginates from *L. digitata*, perhaps because

TABLE III

EFFECT OF METHOD OF PREPARATION ON PROPERTIES OF ALGINATE FROM *L. digitata*
 Alginate was extracted by the basic method and the solution was divided into five parts

Method	Yield of alginic acid, % of air-dried weed	Viscosity, cs.*		Analysis of dried sodium salt	
		(1)	(2)	% alginate†	% sulphated ash
(A) Precipitated with ethanol	27.2	—	5.1	78.7	48.98
(B) Precipitated with calcium chloride, leached with hydrochloric acid at 10°C.	20.6	2.9	2.1	—	33.35
(C) Decolorized with carbon, then as in (A)	17.5	—	7.7	93.4	35.87
(D) Decolorized with carbon, then as in (B)	17.6	3.1	2.3	99.9	34.84
(E) Decolorized with carbon, precipitated with hydrochloric acid at 10°	17.1	5.6‡	3.9	95.1	32.73

* (1) Solutions diluted to 0.25% after titration of alginic acid with sodium hydroxide.

(2) Solutions prepared by weighing out the sodium alginate after drying for a week in vacuo over phosphorus pentoxide.

† Determined by titration, except for sample E which was done by the method of Cameron, Ross, and Percival (3).

‡ With No. 1 viscometer. With No. 2, 4.9 cs.

the weed was air-dried at approximately 25°C. for several days (1). The viscosities were lowered 25–30% by merely precipitating the sodium salt and drying it at room temperature. In general, higher viscosities were noted in solutions after treatment with carbon or even Magnesol than in those without such treatment.

A slow decrease of about 13% in viscosity was observed in a solution of sodium alginate in 0.1 *N* sodium chloride on standing at 20°C.

Bleaching of Alginate from F. vesiculosus

The minimum amount of 1 *N* sodium hypochlorite necessary to decolorize completely 1 gm. of weed in four hours was determined to be about 1 ml. Thirty grams of weed were then extracted by the basic method and the extract bleached as above. The yield of white sodium alginate was 10.4% and the viscosity was only 1.34 cs.

In Table IV are shown the results of experiments in which only partial bleaching was used to avoid excessive loss of viscosity. Yields and viscosities are lower than with unbleached samples. Treatment of the calcium alginate with sulphur dioxide by the procedure of Rose (10) was perhaps unnecessary. Extractions at 10°C. and 23°C. furnished alginate with somewhat higher viscosities and in slightly lower yields than at 60°C.

TABLE IV

EFFECT OF BLEACHING AND TEMPERATURE OF EXTRACTION ON PROPERTIES OF SODIUM ALGINATE FROM *F. vesiculosus*

The alginate was extracted by the basic method, and the crude solutions bleached with 1 *N* sodium hypochlorite, 0.5 ml. per gram of weed. Calcium alginate was then precipitated immediately, and treated on the funnel with 1/10th saturated sulphur dioxide solution for an hour, except in the experiments where no hypochlorite was used and in (8) and (10) as indicated in the footnotes

	Temperature of extraction, °C.	Time of bleaching, min.	Viscosity, cs.		Yield of sodium alginate, % of dried weed	Color of sodium alginate
			No. 1 viscometer	No. 2 viscometer		
(1)	60	0	3.7	3.3	17.5	Ivory
(2)	60	30	5.5	4.9	15.0	White
(3)	60	15	5.2	4.6	14.8	White
(4)	10	0	—	7.2	15.3	Ivory
(5)	10	10	—	5.2	13.1	White
(6)	23	0	—	8.2	15.5	Ivory
(7)	23	10	5.2	4.6	14.9	White
(8)*	23	10	4.9	4.3	15.3	White
(9)†	23	0	—	6.0	16.4	Almost white
(10)‡	23	10	2.5	2.1	(24.3)	Pale yellow

*Sulphur dioxide treatment omitted.

†Sulphur dioxide treatment included, although no hypochlorite was used.

‡After bleaching, the crude sodium alginate was precipitated with four volumes of ethanol. Product was hard, brittle, and very impure, so that the figure for yield was insignificant.

DISCUSSION AND CONCLUSIONS

It has been shown that clear water-white solutions of sodium alginate can be prepared from rockweed. Even without special treatment, much of the color was removed during the extraction with lime water, and this operation was shown to be desirable in other ways. Much color remained in solution when the calcium alginate was precipitated and more was dissolved out if the free freshly prepared moist alginic acid was extensively washed with ethanol. With more thorough washing with ethanol an ivory colored product was obtained. Without extensive treatment with ethanol, the color was pale brown, while the comparable product from *L. digitata* was nearly white.

Decolorization with the usual adsorbents was only partially successful and passage through a carbon-Celite column was the most effective treatment. Exposure to formaldehyde was unsuccessful, although this method has apparently been used previously commercially (9).

It was repeatedly observed that most of the objectionable color developed during the extraction of *F. vesiculosus* with sodium carbonate, in contrast to its absence with *L. digitata*. This development of color could be prevented by prolonged extraction of the weed with methanol or ethanol prior to alkaline extraction. Nearly colorless products were thus obtained with little loss of viscosity.

Bleaching is perhaps best avoided since careful control is necessary to avoid excessive loss of viscosity. Very brief partial bleaching is, however, more satisfactory.

The method of purification has been shown to have profound effect on viscosity, yield, and purity of product. Results agreed in general with earlier studies (1, 4, 10) and confirm the tendency of alginate to depolymerize. Highest viscosities were obtained when no purification was attempted, and when low temperatures of extraction were used. Some of the alginates prepared as above have been compared with commercial products by Vincent, Goring, and Young (11).

Although a satisfactory sodium alginate with viscosity of 3.7 to 8.2 cs. can be prepared readily from *F. vesiculosus* in the laboratory with no special decolorizing treatment, this plant must be regarded as a more difficult source of alginate than the kelps. Indeed, it may be a quite different alginate, as indicated by the recent work of Fischer and Dörfel (6).

ACKNOWLEDGMENTS

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ON THE FRICTION OF HEATED SLEIGH RUNNERS ON ICE UNDER HIGH LOADING¹

By C. D. NIVEN

ABSTRACT

Heating the stainless steel runners on a small model sleigh loaded up to 54 kgm./sq. cm. reduced the friction only slightly but this reduction was most marked when the temperature was low and the speed was low. The results are discussed.

For many years it was assumed that the low friction qualities of ice were to be accounted for by the presence of water between the slider and the ice. Bowden and Hughes (1) pointed out that if this water were present it was more likely to be caused by frictional heating than by pressure. That heat is dissipated at the surface of the ice if a slider is dragged over a level sheet of ice is obviously correct but by explaining the melting of lubrication water in this way no mention was being made of the fact that water expands on freezing.

Some work initiated by the writer and undertaken in this laboratory by Mr. P. M. Pfalzner (5) on the heating of nichrome sleigh runners added some experimental results which complicated rather than clarified the situation. If frictional heating caused the formation of water, which in turn accounted for the low friction of ice, then heating the runner to help form that water would presumably reduce the friction. Pfalzner found that the friction was reduced very little even if a large amount of heat were supplied to the runner. Since Pfalzner's work was published it has been proved (4) that high loading very markedly reduces friction on ice, a result which pointed right back to the old pressure melting theory and of course to that unusual property which water possesses of expanding on freezing.

Since a sleigh with small runner area in contact with the ice would lose less heat to the ice than one of large area under similar temperature conditions, and since the behavior of a sleigh on ice is considerably different at high loading than it is at low loading, the writer thought that some further information might be gained to help clarify matters if a small heavily loaded heated sleigh were used in place of the large heated sleigh which Pfalzner had used. The object of this investigation which is described below was not to measure efficiencies but to observe changes in drag with heating when high loadings were used.

APPARATUS AND METHODS

It was decided to make the runners and the main body of the sleigh out of one piece of stainless steel. This implied supplying a heater instead of simply putting current through runners of high electrical resistance. Fig. 1 shows the

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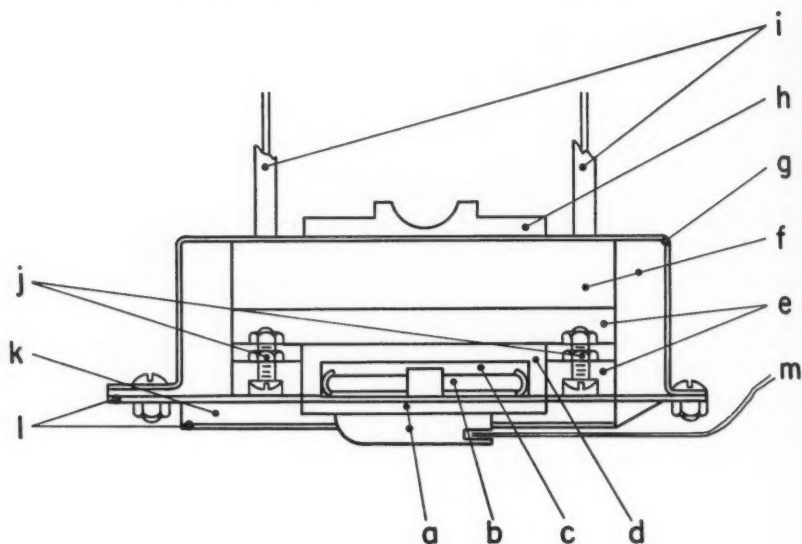


FIG. 1. Drawing of heated sleigh.

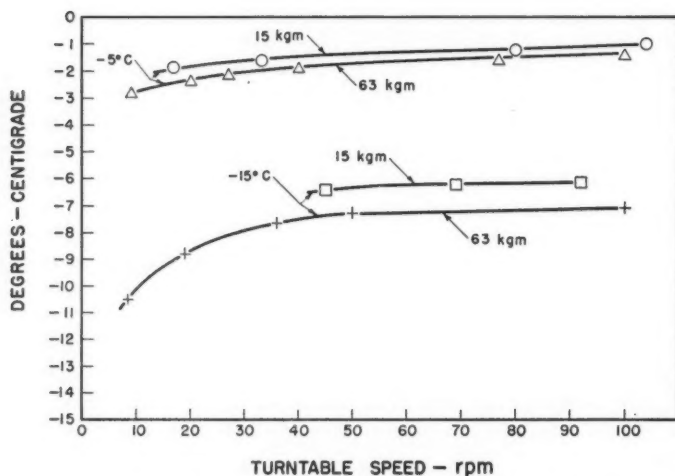
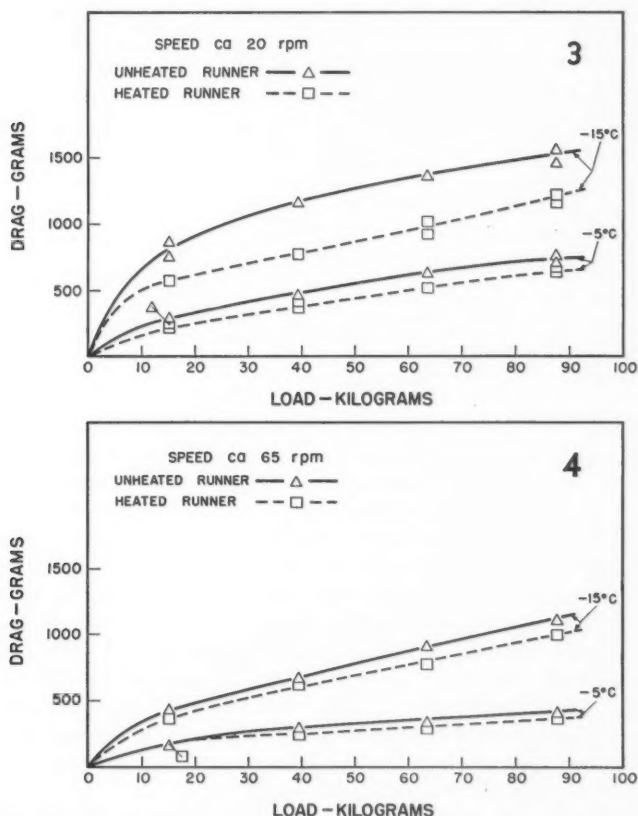


FIG. 2. Curves showing rise of thermocouple temperature with speed at two loadings and at two temperatures.

construction. The sleigh was surrounded by insulation in order to force as much of the heat as possible into the runners. The apparent area of runner in contact with ice totalled 1.6 cm^2 . In Fig. 1, *a* is the stainless steel sleigh, *b* the heater, *c* a cavity made by the brass bridge *d* to keep the load off the heater,

e is high temperature insulation board (transite), *f* onazote insulation, *g* sheet brass casing, *h* a heavy brass plate to take the load from the loading arm of the turn table (4), *i* the lead wires from a variac, *j* brass binding posts to connect the leads *i* with the heater leads, *k* asbestos cloth insulation, *l* sheet brass, and *m* a copper-constantan thermocouple.

The thermocouple was fixed with cutex in a small hole drilled in the rear end of one of the runners about $3/64$ in. from the surface touching the ice: it measured a temperature somewhere between the temperature at the tips of the runner asperities in contact with ice and the temperature of the main body of the sleigh. Therefore when the sleigh was running and no heater current had been applied, one would expect the thermocouple temperature to be somewhere between the temperature of a molten asperity, i.e. 0°C ., and the temperature of the refrigerated room. The curves in Fig. 2 show that this is the case. They



FIGS. 3 AND 4. Drag vs. load curves for unheated and heated sleigh at two temperatures and at a speed of about 20 revolutions per minute (Fig. 3) and of about 65 revolutions per minute (Fig. 4).

also show that the thermocouple temperature increases with either speed or loading, indicating that more heat is thereby generated at the interface. Ice therefore behaves in this respect like a fusible metal (2).

When heat was put into the main body of the sleigh by supplying current to the heater, the heat flow in the runner could be made to change direction, so that instead of heat flowing from the interface to the sleigh, heat flowed from the sleigh to the interface. It was soon found that excessive heat input melted deep grooves in the ice without causing any spectacular change in the drag. This indicated that the best that could be expected from heating the runners was to bring their temperature up to 0°C . at the interface when the sleigh was running. The thermocouple was watched while the heat was being applied, and when a temperature of less than 1°C . was indicated, the drag was measured. Figs. 3 and 4 show the drag vs. load curves without and with heat—Fig. 3 referring to a slow speed of 20 r.p.m. and Fig. 4 to a higher speed of 65 r.p.m.

DISCUSSION OF RESULTS

The results at high loading confirm Pfalzner's (5) two general conclusions that the friction fell very little when the runners were heated and that the benefit derived thereby was considerably greater at low temperature. Figs. 3 and 4 suggest another conclusion, namely, that the reduction in drag was less noticeable at high speed.

Thus in explaining the effect of heating runners the following four facts have to be kept in view:

- (A) A reduction in drag is present.
- (B) It is small.
- (C) High speed tends to wipe it out.
- (D) It is more marked at low temperature.

If the low friction of ice is to be accounted for as Bowden has done by the melting of ice asperities through frictional heating, then (A) is rather to be expected. (B) and (C) state that artificially supplied heat simply cannot get on to the asperities of the ice quickly enough to have very much effect on the drag. Naturally when the speed is high the slowness of the heat flow is accentuated. This inability of the heat to get there fast enough to decrease drag would suggest that heat flow across the interface from slider asperity to ice asperity may be small and so of little account in determining the friction. If this is so, it seems to be a reasonable inference that heat cannot travel fast enough in the reverse direction either to have much influence on the friction. It would appear then that Bowden and Hughes (1) may have attached too much importance to the thermal conductivity of a slider and if so McConica's (3) observation that magnesium slides are better than wood does not introduce any anomaly to upset the frictional heat conception.

In regard to (D) one possible reason why artificial heating of the runners is more effective at lower than at higher temperature is that what little heat flow there is from the slider asperity to the ice asperity would depend on the

temperature difference: assuming a slider asperity temperature of 0°C ., there would be three times as much heat flow when the ice asperity was at -15°C . as at -5°C . The heating current was adjusted to bring the slider asperity to approximately 0°C . If actual drag reductions are considered, diagrams 3 and 4 indicate that the factor 3 is just about right. However, the writer offers this explanation with considerable reserve, because there are other things to complicate the mechanism; for instance cold ice needs more heat to melt it: at the same time the latent heat of fusion remains constant regardless of the temperature of the ice.

The r.p.m. speeds of 65 and 20 correspond roughly to 6 and 2 m.p.h. It can be inferred then that heated sleigh runners would not be of economic importance for mechanical transportation at 20 or more miles per hour. However at 3 m.p.h. there is a possibility that they might be used to advantage in cold weather if some means were provided to prevent the runners from melting in when the sleigh stopped.

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A PORTABLE ELECTRICAL MAGNETOMETER¹

By P. H. SERSON AND W. L. W. HANNAFORD

ABSTRACT

Portable electrical magnetometers, consisting of a magnetic detector of the saturated transformer type mounted on the telescope of a theodolite, have been used by the Dominion Observatory in magnetic surveys since 1947. The use of filters in the electronic equipment is avoided by tuning the detector heads. Comparisons with magnetic standards at Agincourt observatory indicate that the probable error of a single observation (requiring 15 min.) is as follows:

- (a) in declination, $\pm 0.3'$ ($H \sin 0.3' = 3$ gammas),
- (b) in inclination, $\pm 0.2'$ ($F \sin 0.2' = 3$ gammas),
- (c) in total intensity $\pm 0.02\%$ to $\pm 0.1\%$ (± 10 gammas to ± 50 gammas) depending on the frequency of standardization.

INTRODUCTION

A portable electrical magnetometer using a detector of the saturated transformer type was built at the Dominion Observatory in 1947 for use in a survey in the neighborhood of the North Magnetic Pole. With this instrument it proved possible to make a complete observation of declination, inclination, and total intensity in 15 min. at any magnetic latitude. Further development has resulted in simpler and more stable circuits. Nine of the magnetometers are now used in occupying magnetic stations in all parts of Canada and at some of the permanent magnetic observatories.

GENERAL DESCRIPTION

The field-sensitive unit, or detector head, is mounted on the telescope of a non-magnetic theodolite, with its axis of sensitivity parallel to the optical axis of the telescope. The detector head is connected by a six-conductor cable 30 ft. long to a control box, which must be kept at a distance from the point of observation because of magnetic parts. On the front of the control box is a center-zero meter which indicates the magnitude and sense of the component of the geomagnetic field along the axis of sensitivity of the detector. The sensitivity of the meter indication is usually set at 30 gammas full scale. A large positive lens mounted in front of the meter makes its reading clearly visible from the theodolite. A portable potentiometer, used in measurements of intensity, is connected to the control box by a short cable (Fig. 1).

THE MAGNETIC DETECTOR HEAD

The detector head is of the saturated transformer type first described by Vacquier (1). It contains two strips of Mumetal $4.0 \times 0.10 \times 0.014$ in., mounted side by side with their long axes parallel to the optical axis of the telescope.²

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Contribution from the Department of Mines and Technical Surveys, Ottawa, Canada. Published by permission of the Acting Deputy Minister.

²After being cut to size, the Allegheny Mumetal strips were held at 1100°C . for two hours, cooled to 800°C . in one-half hour, and then cooled to 580°C . in eight hours in a continuous flow of dry hydrogen.

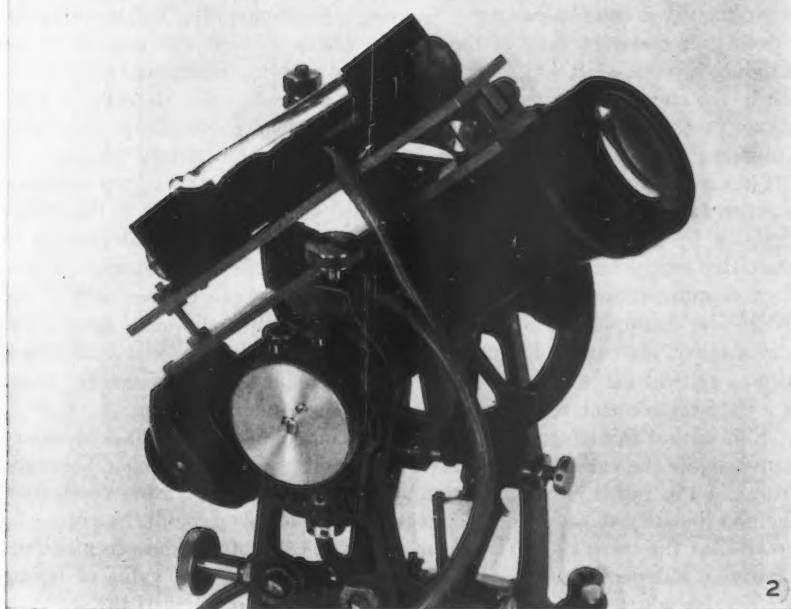
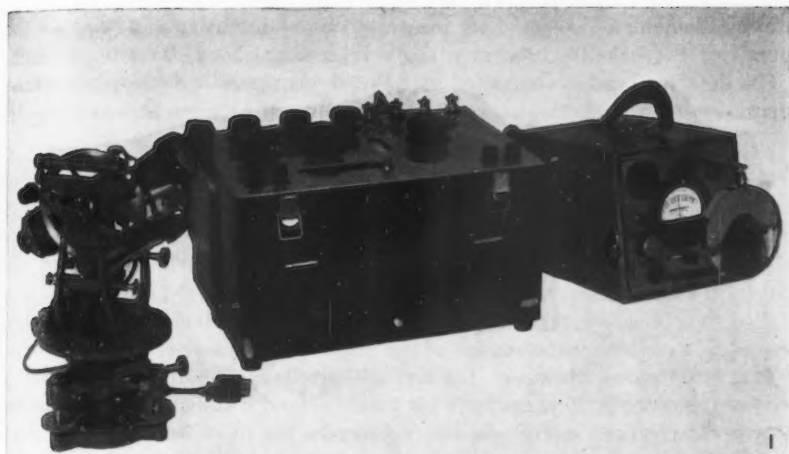


FIG. 1. Portable electrical magnetometer.

FIG. 2. Detector head.

Each strip is surrounded by a primary coil consisting of a single layer of number 30 wire, closely wound. The primary coils are connected in series opposition to a source of 1000 cycle alternating current. The two Mumetal strips with their primaries are slipped into a common secondary coil of about 3000 turns of number 30 wire. The whole unit is mounted in a bakelite tube of 0.375 in.

internal diameter. A solenoid for measurement of intensity is wound on the outside of the bakelite tube in a single layer with about 80 turns per inch.

The detector head is supported by bakelite clamps on a brass plate whose orientation relative to the telescope can be adjusted by three screws (Fig. 2).

THE MAGNETIC DETECTOR CIRCUIT

The balanced detector described above gives an output signal composed of even harmonics of the frequency of the oscillator supplying the excitation current. The amplitude is proportional to the component of the earth's field along the axis of the coils, provided this component is small, and the waveform inverts when the sign of the component is reversed. If the signal is applied to a phase-sensitive detector whose reference is double the excitation frequency, a center-zero indication of the magnitude and sign of the component of field is obtained. However, the second harmonic content of the signal is low—of the order of 10 microvolts per gamma—and if sufficient amplification to give the required meter sensitivity precedes the phase-sensitive detector, the amplifier and detector are saturated by the higher harmonics of the signal. This difficulty is usually overcome by using a band-pass filter to attenuate the undesired frequencies. Any of the simpler filters with enough discrimination introduce a phase-shift which changes rapidly with frequency and with variation in the components of the filter. When a phase-sensitive detector is used, this uncertain phase-shift presents a serious problem, particularly in portable equipment subject to large changes in temperature and battery voltage.

It has been found possible to avoid the use of filters by tuning the magnetic detector. If the secondary coil of the Vacquier detector is tuned to the second harmonic by a condenser connected across its terminals, a great increase in sensitivity occurs as well as a relative reduction in the other harmonics. The effect is quite different from that of a tuned inductance elsewhere in the circuit—for example, infinite sensitivity and 'more than infinite' sensitivity, or instability, are easily obtained if the resistance of the secondary winding is below a critical value. The sensitivity can be reduced to a convenient value by a rheostat connected as a shunt across the secondary.

To show that this effect can be used in a practical instrument, it is necessary to investigate the variation in the sensitivity and phase of the second harmonic output of the tuned detector for small changes in the operating conditions. The non-linearity of the Mumetal cores makes analysis difficult, but it can be shown that the cores should be saturated for 28.5% of the time to make the sensitivity independent of excitation amplitude. There is a value of tuning capacity for which the sensitivity is independent of frequency. If the shunting resistance is adjusted for infinite sensitivity with the optimum excitation and capacity, it can be calculated that for variations of $\pm 5\%$ in the excitation current, $\pm 5\%$ in the excitation frequency, $\pm 10\%$ in the tuning capacity, and $\pm 10\%$ in the shunt resistance, the sensitivity of the detector will remain above 1 millivolt per gamma. With the above changes in operating conditions, the variations in the phase of the detector output relative to the excitation phase are 1.2° , 0.5° , 0.5° , and 0.9° respectively. Adequate sensitivity to indicate

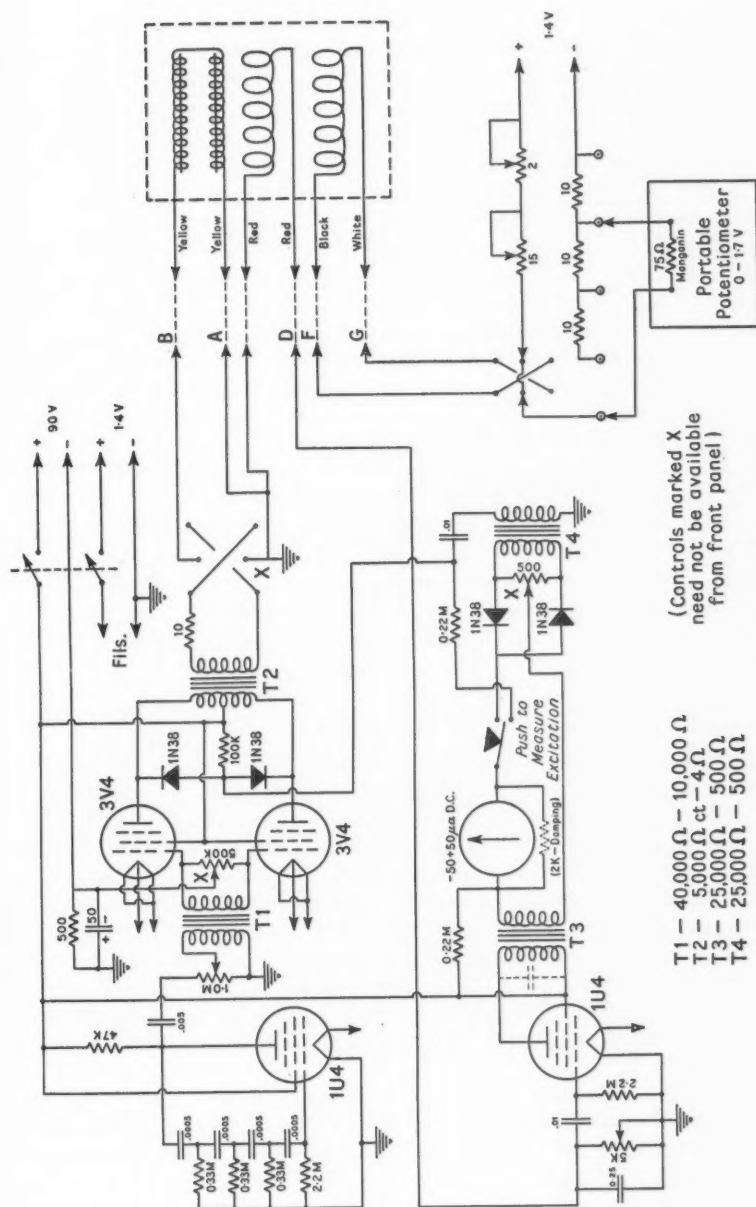


FIG. 3. Portable magnetometer circuit.

1 gamma is easily obtained with one stage of amplification of the detector output.

The circuit of a typical instrument is shown in Fig. 3. A phase-shift oscillator feeds a push-pull amplifier to supply the 1000 cycle excitation. The germanium diodes in the plate circuit of this amplifier provide the 2000 cycle reference signal for the phase-sensitive detector as well as acting as an output rectifier for reading excitation amplitude.

The two Mumetal strips in the detector heads and their primary windings are never identical. If they are unbalanced by 1%, and the excitation current contains 1% of second harmonic, a second harmonic signal will be induced in the secondary coil with an amplitude of about 30 gammas when the detector is in zero steady field. The result is that the indicated null is displaced from the true null by some 30 gammas. This zero error appears in the angle read from the theodolite in the case of declination or inclination measurements, and in the voltage read from a potentiometer in the case of intensity measurements, but is eliminated in the mean indicated null of a set of observations as described in the next section. Such a zero error, while it has no effect on the accuracy of the observations if constant, is annoying to the operator. In the circuit shown, an adjustment—the potentiometer between the grids of the driver amplifier—is provided for removing even harmonics from the excitation. The potentiometer is adjusted until the indication of the center-zero meter remains unchanged when the excitation current is reversed by the switch in the primary circuit. Alternatively, the switch may be omitted, and the adjustment made to equalize the pair of readings obtained in a total intensity measurement.

OBSERVING PROCEDURE

To measure declination the theodolite is levelled and the vertical circle is set at zero, so that the axis of the detector is approximately horizontal. The upper part of the theodolite is turned about the vertical axis until the meter indicates a null, and the horizontal circle is read. A second null is obtained by rotating the theodolite 180° in azimuth. The telescope is then inverted and two more readings obtained. The mean of the four readings is the horizontal circle reading of the magnetic meridian, since the procedure has eliminated errors due to lack of perpendicularity of the sensitive axis of the detector to the axes of the theodolite as well as the error due to any constant zero-error of the null indication. The horizontal circle reading of the true meridian is obtained in the usual way by astronomical observations using the same theodolite.

Inclination is measured by tilting the telescope about the horizontal axis in the plane of the magnetic meridian until a null is indicated. Four readings of the vertical circle are obtained by inverting the telescope and rotating the theodolite 180° in azimuth.

Now that the orientation of the magnetic vector is known, the axis of the detector can be set parallel to it. A direct current passing through a solenoid

wound on the detector head is varied until a null is indicated. The direct current is then proportional to the total intensity, the constant of proportionality depending on the geometry of the detector head. The current is measured by measuring the potential difference across a manganin resistor in the circuit by means of the portable potentiometer. Zero error is eliminated by repeating the observation with the telescope reversed. Two further measurements serve as a check. A typical observation is shown in Fig. 4.

DOMINION OBSERVATORY MAGNETIC OBSERVATIONS									
Stn.	Agincourt			Sensitivity	208	Date	May 16 1955		
Instr.	# 12					Lat.			
Obs'r.	W. H.					Long.			
DECLINATION						Chr. G. M. T.			
Coil	Circle N.	Circle S.	Mean	Mark		Begin	End		
Up	17 44.0	197 44.2	44.1	118 07.8		1454			
Dn	17 19.2	197 01.8	10.5	299 07.8			1458		
Mn	31.6	23.0	17 27.3	299 07.8		Mean	1456		
	Mag. N.	107 27.3	Az.	183 26.3					
	True N.	114 41.5	T.N.	114 41.5					
	Corr'n.					G.M.T.			
	Decl.	7 14.2	W			L.M.T.			
INCLINATION						Chrono.			
Coil	Circle E.	Circle W.	Mean			Begin	End		
Up	15 27.8	25.0	26.4			1459			
Dn	24.6	27.8	26.2				1503		
Mn	26.2	26.4	15 26.3						
Inclination	74 33.7						1501		
Pot. Readings			TOTAL		Temps.		Chrono.		
Obj.	Circle E.	Circle W.	Mean	Coil	Pot. Cell	Begin	End		
Up	1.0594	1.0596	1.0595	E. 22.0	---	1504			
Dn	1.0586	1.0594	1.0585	W. 22.0	---		1508		
Mn	90	90	1.0590				1506		
Log R	0.02490			L Sin I	T.59404				
Log C	1.61723			Log F	T.76633				
Log P	2.12420			Log Z	T.75037				
Log F	T.76633		F 58389						
L Cos I	T.42521								
Log H	T.19154		H 15343						
L Tan I	0.55884								
Log Z	T.75037		Z 56282						

FIG. 4.

COMPARISONS WITH STANDARDS

Total intensity F is calculated from the equation $F = PCR$, where P is the constant of the potentiometer and resistor combination (in amperes per volt), C is the constant of the solenoid (in gauss per ampere), and R is the potentiometer reading in volts.

The potentiometers and manganin resistors are compared electrically with laboratory standards to determine P with a probable error of 2×10^{-5} to 8×10^{-5} , depending on the type of potentiometer. The solenoid constant C can be computed with a similar probable error by a comparison of total intensity observations at a magnetic observatory with the total intensity computed from the magnetograms.

A temperature correction is applied to C by the formula $\log_{10} C_t = \log C_{20} - 2.5 \times 10^{-5}(t - 20)$, where the temperature of the detector is $t^\circ\text{C}$. A correction to P for the temperature of the standard cell may be necessary, depending on the design of the potentiometer.

It soon became apparent that the constants of the instruments changed with time, and a program of measurements to locate the source of the change was started in 1953.

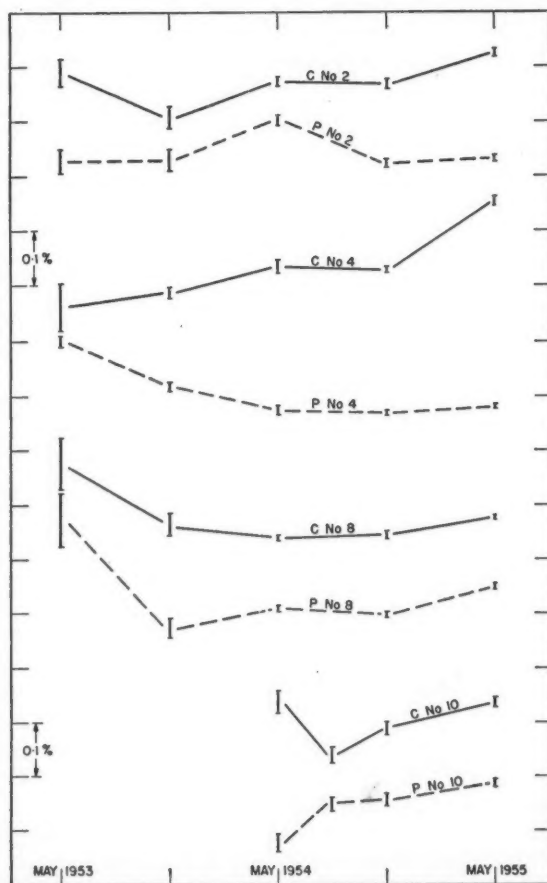


FIG. 5. Change of constants of magnetometers Nos. 2, 4, 8, and 10. The length of the vertical line indicates the probable error of the measurement.

RESULTS OF COMPARISONS

Approximately 50 comparisons of the portable magnetometers with the observatory standards at Agincourt have been made, each comparison including 10 or 12 observations with an instrument. The probable error of a single observation (including the error in reading the magnetograms) is $\pm 0.3'$ in declination and $\pm 0.2'$ in inclination, corresponding to ± 3 gammas at Agincourt. On every occasion when systematic differences have been observed greater than $0.5'$ in declination and $0.2'$ in inclination between an instrument and the Agincourt standards, the cause has been traced to the presence of magnetic material—usually to the portable potentiometers with their associated galvanometers. It is concluded that no corrections need to be applied to the inclination and declination readings.

Some typical changes in the solenoid constant C and the potentiometer constant P for four instruments over a two-year period are shown in Fig. 5. It will be seen that over six months changes of 1 part in 1000 in both P and C can occur—changes much larger than the probable errors of the standardizations.

The variation in P is larger than would be expected in equipment of this type, and it was investigated further. Occasionally, changes were traced to the manganin resistor, but more often the standard cells were responsible. To overcome this difficulty, potentiometers with three standard cells are now being used, but figures on their performance are not yet available.

CONCLUSIONS

With the portable electrical magnetometer one observer can measure declination, inclination, and total intensity in 15 min. at any magnetic latitude. The probable error of a single observation in determining the orientation of the earth's field is ± 3 gammas ($\pm 0.3'$ in declination in southern Canada, $\pm 0.2'$ in inclination). Immediately after standardization, the probable error of a single observation of total intensity is $\pm 2 \times 10^{-4}$ (10 gammas), but over several months changes in the constants of the instrument may produce systematic errors of $\pm 1 \times 10^{-3}$ (50 gammas).

APPENDIX. THEORY OF THE TUNED MAGNETIC DETECTOR

The circuit of a magnetic detector is shown in Fig. 6(a). Assume that the magnetic properties of each of the Mumetal cores can be described by

$$\begin{aligned} \partial B / \partial H &= \frac{1}{2} \mu_0 \text{ for } |H| < H_s, \\ \partial B / \partial H &= \frac{1}{2} \mu_1 \text{ for } |H| > H_s, \end{aligned}$$

as shown in Fig. 6(b). The fields due to the excitation current in the primary coils are $H_e \sin \omega t$ for one core and $-H_e \sin \omega t$ for the other, where $H_e > H_s$. Let H be the sum of the components along the axis of the cores of all other magnetic fields present. Since $H \ll H_s$, it can be assumed as a first approximation that the cores become saturated and unsaturated simultaneously. Then

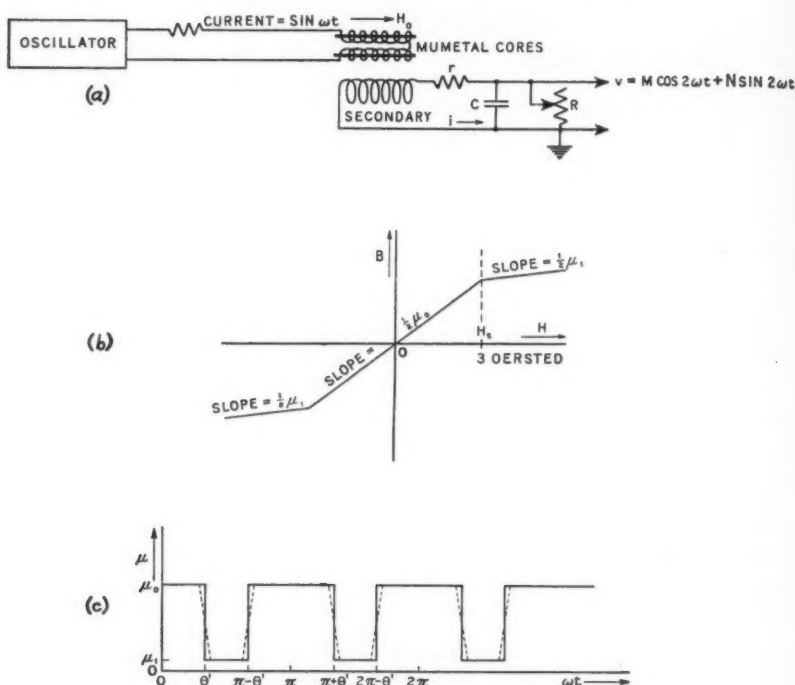


FIG. 6. (a) Magnetic detector. Rheostat R should be labelled S.
 (b) Assumed properties of Mumetal cores.
 (c) Effective permeability of core assembly.

the two cores with their primary windings can be considered as a single piece of ferromagnetic material whose magnetic properties are described by

$$[2] \quad B = \mu(t)H \quad \text{and} \quad \dot{B} = \mu(t)\dot{H} + \dot{\mu}(t)H,$$

where

$$\mu(t) = \mu_0 \quad \text{for} \quad m\pi - \theta' < \omega t < m\pi + \theta',$$

$$m = 0, 1, 2, 3, \text{ etc.},$$

$$\mu(t) = \mu_1 \quad \text{at all other times, and}$$

$$\sin \theta' = H_s/H_c \quad (\text{Fig. 6(c)}).$$

This time-dependent permeability can be expressed as a Fourier series:

$$[3] \quad \mu(t) = \frac{1}{2}a_0 + \sum a_n \cos n\omega t \quad n = 2, 4, 6, \text{ etc.}$$

where

$$a_0 = \frac{4}{\pi}(\mu_0 - \mu_1)\theta' + 2\mu_1,$$

and

$$a_n = \frac{1}{n} \frac{4}{\pi}(\mu_0 - \mu_1) \sin n\theta'.$$

When the secondary coil is shunted by a capacitance and a resistance, alternating current flows in the winding producing a magnetic field of the same order of magnitude as the field to be detected. If

A is the constant of the secondary coil,

c is the tuning capacitance,

H_0 is the magnetic field to be detected,

i is the current in the secondary,

r is the resistance of the secondary,

S is the shunt resistance,

v is the output signal voltage of the detector,

k is the constant of electromagnetic induction,

we have the relations

$$[4] \quad H = Ai + H_0,$$

$$[5] \quad i = c\dot{v} + v/S,$$

$$[6] \quad v = -k\dot{B} - ir.$$

Combining equations [2], [4], [5], and [6] we obtain the differential equation

$$[7] \quad Akc\ddot{v} + \left(Akc\dot{v} + \frac{Ak}{S}\mu + rc \right)\dot{v} + \left(\frac{Ak}{S}\dot{\mu} + \frac{r}{S} + 1 \right)v = k\dot{\mu}H_0.$$

Since μ has a frequency of 2ω , the steady-state solution of [7] for v can be expressed as a Fourier series in even harmonics of the excitation frequency ω . When the detector is tuned to the second harmonic, the terms in 2ω of this series will be larger than the others, and we write the approximate solution

$$[8] \quad v = M \cos 2\omega t + N \sin 2\omega t,$$

an approximation which allows the equation to be solved by straightforward algebraic methods. By substituting for μ and v in equation [7] the expressions given by [3] and [8] and writing $k = 1/2\omega^2 Aa_0c_0$ (c_0 is the capacity which tunes the detector to second harmonic when the excitation current is small or zero), we obtain two equations in M and N whose solutions are

$$[9] \quad M = -\frac{1}{\Delta} \left[\frac{1 - a_4/a_0}{2\omega Sc_0} + 2\omega rc \right] \frac{1}{\omega A c_0} \frac{a_2}{a_0} H_0,$$

$$[10] \quad N = \frac{1}{\Delta} \left[1 - \frac{c}{c_0} \left(1 - \frac{a_4}{a_0} \right) + \frac{r}{S} \right] \frac{1}{\omega A c_0} \frac{a_2}{a_0} H_0,$$

where

$$[11] \quad \Delta = \left[1 - \left(\frac{a_4}{a_0} \right)^2 + 4\omega^2 r^2 c_0^2 \right] \left(\frac{c}{c_0} \right)^2 - 2 \frac{c}{c_0} + \frac{1 - (a_4/a_0)^2}{4\omega^2 c_0^2} \left(\frac{1}{S} \right)^2 + \left(1 + \frac{r}{S} \right)^2.$$

As in the case of any tuned inductance, the response of the system becomes large when the denominator Δ in [9] and [10] is small. Here, however, the presence of the terms in a_4/a_0 in the denominator allows Δ to become zero or even negative.

The condition for infinite sensitivity is $\Delta = 0$, or $c = c_\infty$, where

$$[12] \quad \frac{c_\infty}{c_0} = \frac{1 \pm \sqrt{1 - \left[1 - \left(\frac{a_4}{a_0}\right)^2 + 4\omega^2 r^2 c_0^2\right] \left[\frac{1}{4\omega^2 c_0^2} \left(1 - \left(\frac{a_4}{a_0}\right)^2\right) \left(\frac{1}{S}\right)^2 + \left(1 + \frac{r}{S}\right)^2\right]}}{1 - (a_4/a_0)^2 + 4\omega^2 r^2 c_0^2}$$

Since c_∞/c_0 must be real,

$$[13] \quad \left[\frac{1}{4\omega^2 c_0^2} \left(1 - \left(\frac{a_4}{a_0}\right)^2\right) + r^2 \right] \left(\frac{1}{S}\right)^2 + \frac{2r}{S} + 1 - \frac{1}{1 - (a_4/a_0)^2 + 4\omega^2 r^2 c_0^2} \leq 0$$

or $S \geq S_{\text{critical}}$, where

$$[14] \quad \frac{1}{S_{\text{critical}}} = \frac{-r \pm \sqrt{r^2 - \left[\frac{1}{4\omega^2 c_0^2} \left(1 - \left(\frac{a_4}{a_0}\right)^2\right) + r^2 \right] \frac{4\omega^2 r^2 c_0^2 - (a_4/a_0)^2}{1 - (a_4/a_0)^2 + 4\omega^2 r^2 c_0^2}}}{\frac{1}{4\omega^2 c_0^2} \left(1 - (a_4/a_0)^2\right) + r^2}$$

For S_{critical} to be real and positive,

$$[15] \quad r < \frac{1}{2\omega c_0} \left| \frac{a_4}{a_0} \right|,$$

since $|a_4/a_0| < 1$.

It has been shown that within a range of operating conditions defined by [14] and [15] there are values c_∞ of the tuning capacity for which the sensitivity of the detector is infinite. We must now find the operating conditions under which the sensitivity is high and remains as high as possible with small variations in the frequency and in the amplitude of the excitation current. We confine our attention to the denominator Δ in [9] and [10], since it is much more critical to operating conditions than either numerator.

For a given secondary coil and capacity c , the condition for minimum dependence of sensitivity on frequency is obtained when the roots c/c_0 of the equation $\Delta = 0$ are equal; that is, when $S = S_{\text{critical}}$. Then

$$[16] \quad \frac{c_\infty}{c_0} = \frac{1}{1 - (a_4/a_0)^2 + 4\omega^2 r^2 c_0^2},$$

and when $c/c_0 = (1 \pm \delta)c_\infty/c_0$,

$$[17] \quad \Delta = (c_\infty/c_0)\delta^2 \approx \delta^2 \quad (\text{Fig. 7(a)}).$$

The requirement for independence of Δ from changes in excitation amplitude is filled when $\partial(a_4/a_0)/\partial\theta' = 0$. For annealed Mumetal, $\mu_1 \ll \mu_0$, and we may write $a_2/a_0 = (\sin 2\theta')/2\theta'$ and $a_4/a_0 = (\sin 4\theta')/4\theta'$. Thus the derivative of a_4/a_0 is zero for $\tan 4\theta' = 4\theta'$, or $\theta = 64.4^\circ$, and Δ is unaffected by small changes in the amplitude of the excitation current when the excitation field is about 10% greater than the field at which the cores saturate (Fig. 7(b)). The figures quoted for variation in sensitivity and phase of the output signal were deduced from these equations.

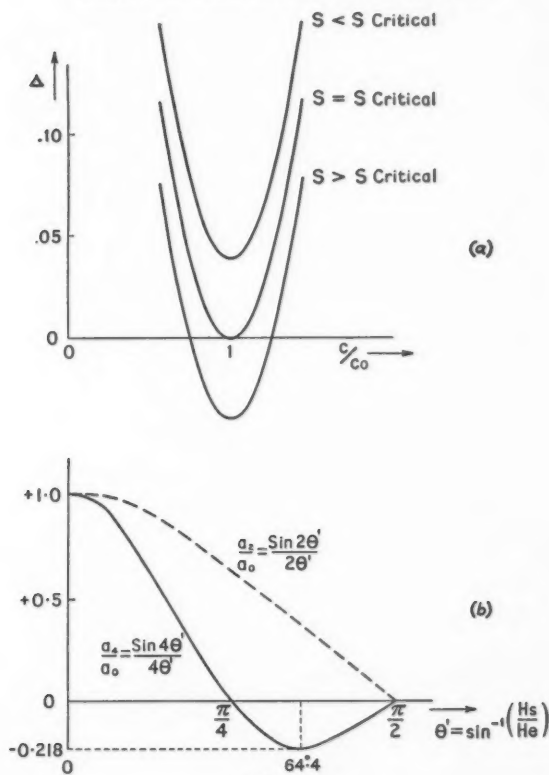


FIG. 7.

To understand the instability of the detector when $S > S_{\text{so}}$, it is necessary to consider the effect of the current in the secondary winding on the instant of saturation of the cores. In the presence of an output signal v , one core saturates before the other, altering the function $\mu(t)$ as shown by the dotted lines in Fig. 6(c). It can be shown that the coefficient a_4 in the Fourier expansion of $\mu(t)$ is modified by the factor $(1 - Kv^2)$ where K is a positive constant. When this factor is included in equation [11], it will be seen that the denominator Δ increases algebraically in the presence of an output signal. If Δ is positive for zero signal, the sensitivity will decrease with increasing signal; if Δ is negative for zero signal, the sensitivity will increase with increasing signal. Thus, if Δ is negative and small for zero signal, a small magnetic field will produce a signal which quickly increases until it is limited by the non-linearity of the cores. This large signal will then persist when the magnetic field is reduced to zero or even reversed.

REFERENCE

1. VACQUIER, V. V. and GULF RESEARCH DEVELOPMENT COMPANY. U.S. Patent No. 2406870. 1946.



